SYNOPSIS

INHIBITIVE ACTION OF *COCOS NUCIFERA* L. (COCONUT PALM) AND *BORASSUS FLABELLIFER* L. (PALMYRA PALM) – SHELL, LEAF STALK AND PEDUNCLE EXTRACTS ON THE CORROSION OF MILD STEEL IN ACIDIC MEDIA AND THEIR ADSORPTION CHARACTERISTICS

Submitted

by

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INTRODUCTION

The studies of mild steel corrosion in acidic media receive more and more attention both of academics and industrialists because of wide applications such as acid pickling, industrial cleaning, acid descaling, in oil recovery and the petrochemical processes. Acid solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing, require the use of corrosion inhibitors in order to restrain their corrosion attack on metallic materials. Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion can be controlled by suitable modifications of the environment which in turn stifle, retard or completely stop the anodic or cathodic reactions or both. This is achieved by the use of inhibitors.

Many synthetic compounds offer good anticorrosive action; but most of them are highly toxic to both human beings and environment. In recent years, plant extracts and oils have become important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention. Attention has been focused on the corrosion inhibiting properties of plant extracts because plant extracts serve as incredibly rich sources of naturally synthesized chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable sources of materials and can be extracted by simple procedures.

Many plant extracts such as *Fenugreek* (Ehteram A.Noor, 2007), *opuntia* extract (El-Etre, 2003) have been studied for the corrosion inhibition of mild steel in acid media. Some of the seeds extract such as *Strychnos Nuxvomica* (Ambrish Sing et al, 2010), *Areca catechu* (Vinod Kumar et al, 2011). The gum extract of *Raphia hookeri* (Umoren et al, 2009) have also been analyzed for corrosion inhibition properties.

The role of an inhibitor is to form a barrier of one or several molecular layers against acid attack. This protective action is often associated with

chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. Sulphur and/or nitrogen containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors. These inhibitors have also found useful application in the formulation of primers and anti-corrosive coatings.

In green corrosion inhibitors, organic substances containing polar functions with nitrogen, sulphur, and/or oxygen in the conjugated system have been reported to exhibit good inhibiting properties. The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction centre for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions.

The present research work aims at establishing the effectiveness of aqueous extract of Shell, Leaf Stalk and Peduncle of *Cocos Nucifera* L. (CN) and *Borassus Flabellifer* L. (BF) -obtained by destructive distillation -as corrosion inhibitors in 0.5 M H_2SO_4 and 1 M HCl media (12 inhibitor systems) using mass loss measurements at various time and temperature. The influence of temperature on adsorption and inhibition efficiency has been studied. Kinetic and thermodynamic parameters that govern corrosion and inhibition processes have been evaluated.

OBJECTIVES

The purpose of the present research work is

- To evaluate the role of shell, leaf stalk and peduncle of CN and BF aqueous extracts obtained from destructive distillation as corrosion inhibitors.
- To establish the effectiveness of CN and BF extracts as corrosion inhibitors.

- To study the effect of temperature on the corrosion process in the absence and presence of extracts by weight loss method in 0.5 M H_2SO_4 and 1 M HCl.
- To find out the phytochemical constituents present in shell, leaf stalk and peduncle of CN and BF using GC-MS and FT-IR.
- To fit a suitable adsorption isotherm for the above experimental data.
- To assess the inhibition efficiency using electrochemical techniques – Tafel intercept method, LPR method and impedance spectroscopy method.
- To compare the performance of the inhibitors by weight loss method and electrochemical techniques.
- To suggest a possible mechanism for the inhibition process.
- To analyse the surface morphology of mild steel in the absence and presence of investigated inhibitors in acid media.

EXPERIMENTAL DESIGN

To assess the inhibitive action of shell, leaf stalk and peduncle of CN and BF extracts, the following studies and techniques were employed.

Selection of Sample

Mild steel is a structural material of choice to fabricate various reaction vessels, pipes and so on in sugar, petrochemical, textile, food, paper and marine industries. Mild steel suffers from severe corrosion in aggressive environment which need to be protected. Mild steel specimen with the following chemical composition in wt % C, 0.11; Si, 0.061; Mn, 0.197; S, 0.023; P, 0.025; Ni, 0.010; Mo, 0.013; Cr, 0.037; Fe, 99.524; were used for the study.

Selection of Acid Media

Hydrochloric acid and Sulphuric acid are widely used as pickling agents for the removal of rust and scale in several industrial processes. Hence HCl and H_2SO_4 were used for the study.

Selection of the Inhibitor

The use of natural products otherwise tagged “green corrosion inhibitors” has been advocated because of

- ✓ Its inexpensive nature
- ✓ High recoverability, and the most important thing is, they are not petroleum derivatives.
- ✓ Non toxic nature.
- ✓ Environmentally acceptable.
- ✓ Readily available.
- ✓ Non-hazardous.
- ✓ A renewable source for a wide range of inhibitors needed.

Plant extracts are incredibly rich sources of naturally synthesized chemical compounds (*e.g.* amino and organic acids, glucosinolates, alkaloids, polyphenols, tannins) and most are known to have inhibitive action.

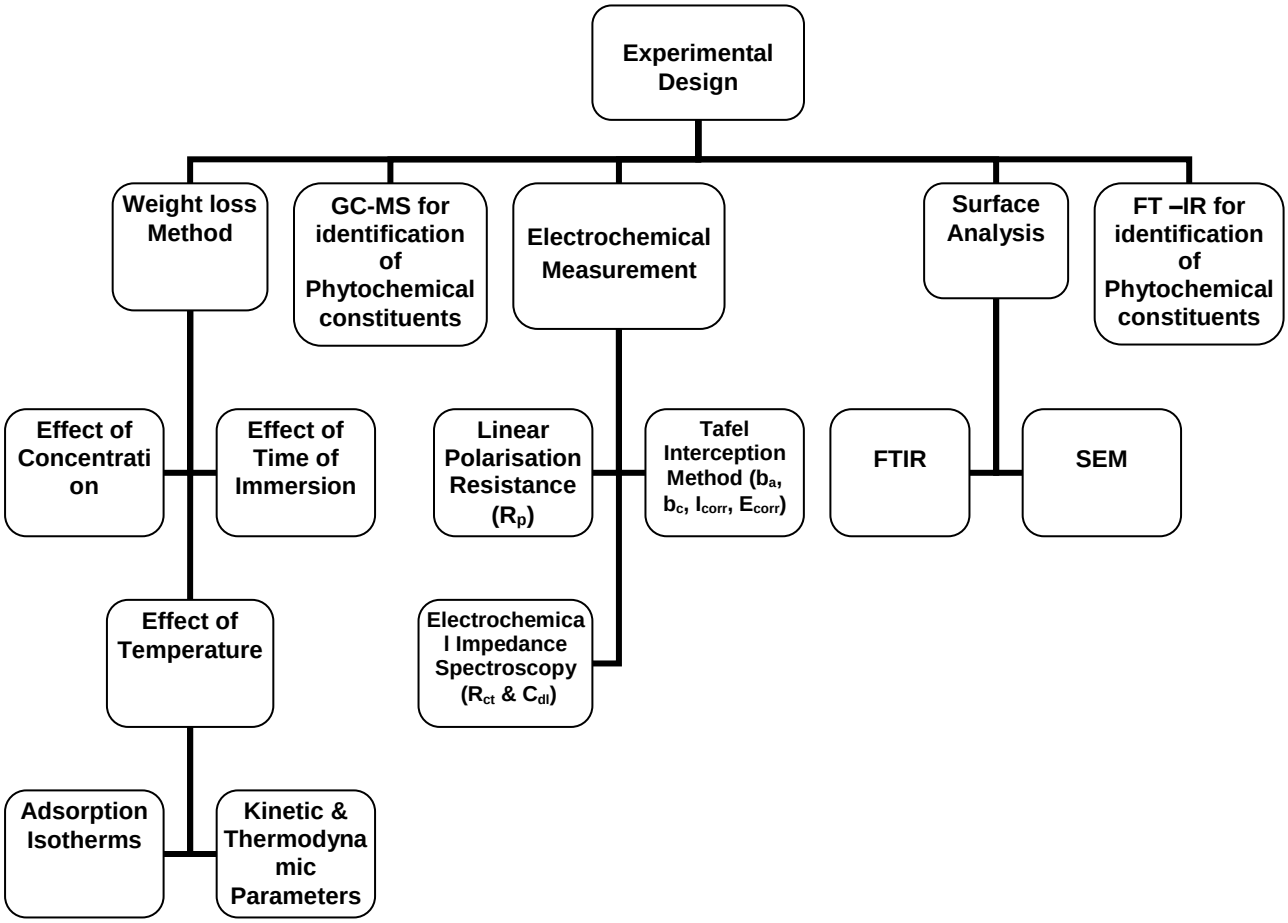
Preparation of CN and BF Extracts by Destructive Distillation Method

Destructive distillation is a process in which wood is heated to form charcoal and OH derivatives. Wood pieces such as shell, leaf stalk and peduncle of CN and BF, respectively placed into a 2000 round bottomed flask and it was connected to water condenser and heated with the help of heating mantle. The gas leaving the apparatus contains the material largely in vapor form. As the wood is heated at 70 to 80˚C, it becomes darker, beginning to char. The wood is decomposing, and one of the decomposition products is methanol, other products also vaporize from the wood. A beaker is placed over the end of the water condenser, so that the vapors coming out will condense on this beaker. Brown liquid is forming from the vapors that condense. By destructive distillation of wood it is possible to produce the combustible vapor, methyl or wood alcohol. The charcoal left behind is much higher in carbon content than the carbohydrate of the original wood.

In this way, the building blocks of many natural materials were deduced from the fragments generated from their thermal degradation. Destructive distillation is not a unit operation like distillation, but a set of chemical reactions.

The process entails the “cracking” (breaking up) of macromolecules into smaller, more volatile, components. Destructive distillation remains a viable route to many compounds, and it has emerged as a possible route for recycling of monomers derived from waste polymers. The extracts were characterized by GC-MS and IR spectral studies.

Techniques Adopted



Weight Loss Measurements

Weight loss measurements were performed by immersing the mild steel coupons into acid solution (100 mL) without and with various amounts of inhibitors at different periods of immersion. After the elapsed time, the specimen were taken out, washed, dried and weighed accurately. All the experiments were performed in triplicate.

Electrochemical Measurements

Electrochemical studies were carried out using Solatron electrochemical analyzer (model 1280 B) interfaced with an IBM computer was used for measurements.

Surface Analytical Techniques

Surface examination of the iron substrate in the presence and absence of the inhibitor was carried out by JOEL MODEL JSM 6360 **Scanning Electron Microscope**. The interaction between the phytochemical compounds and the metal surface has been studied by **FTIR spectrum.** The FTIR spectrum was recorded with a frequency ranging from 4,000 to 400 cm^{-1} using BRUKER Optik GmbH FTIR spectrometer MODEL No - TENSOR 27 with the SOFTWARE - OPUS version 6.5 (CECRI – India).

SALIENT FEATURES

The salient features pertaining to the present study entitled “Inhibitive action of *Cocos Nucifera* L. (Coconut Palm) and *Borassus Flabellifer* L. (Palmyra Palm) – Shell, Leaf stalk and Peduncle extracts on the corrosion of mild steel in acidic media and their adsorption characteristics” are summarized below:

1. The investigated inhibitors, performed in an effective manner to minimize the corrosion of mild steel in both acidic media.
2. Analysis of the results of the weight loss measurement infer that the inhibition efficiency increased with increasing concentration of shell, leaf stalk and peduncle of CN and BF, respectively.
3. The inhibitors could furnish the following efficiency at a maximum concentration of 3%v/v – 98.5% and 98.0% in 0.5 M H_2SO_4 and in 1 M HCl in the presence of CNS, 98.4% and 96.3% in 0.5 M H_2SO_4 and 1 M HCl in the presence of CNLS, 97.6% and 97.5% in 0.5 M H_2SO_4 and 1 M HCl in the presence of CNP, 97.6% and 98.1% in 0.5 M H_2SO_4 and 1 M HCl in the presence of BFS, 98.6% and 97.6% 0.5 M H_2SO_4 and 1 M HCl in the presence of BFLS, 97.0% and 97.8% in 0.5 M H_2SO_4 and 1 M HCl in the presence of BFP, respectively .

4. Immersion studies reveal that, as the time of immersion increased from ½ hr to 24 hrs the inhibition efficiency increased, thereby indicating the enhanced stability of the adsorbed constituents of the extract on mild steel surface, at longer periods of immersion. All the investigated inhibitors could afford a maximum IE in the range of 90-98% in both acid medium. It is obvious that the studies inhibitors are promising inhibitors in 0.5 M H_2SO_4 and 1 M HCl at various time of immersion.
5. All the inhibitors used in the current study reveal that inhibition efficiency increased with increase upto a particular temperature (313 K) and then decreased at higher temperatures. Maximum IE for all investigated inhibitors was found to be around 90%. This may be due to the adsorption of the inhibitor upto particular temperature (313 K) and then desorption of the inhibitor at higher temperature.
6. In the present investigation E_a values were found to be greater/smaller than those calculated in the absence of the inhibitors. This can be explained by the fact that, at high degree of coverage, the dissolution process is not only determined by the reaction of the metal from the bare surface but also involves the adsorbed inhibitor.
7. All the studied inhibitors furnish a large negative value of free energy of adsorption. In the present study, the calculated values of ΔG^{o}_{ads} obtained for CN and BF extracts in both the acid media ranges between 11 kJ/mol and 16 kJ/mol, indicating that the adsorption of CN and BF extracts on mild steel in acid solution was spontaneous.
8. The values of ΔH_{ads} were found to be negative for the following inhibitor systems - BFS and BFP in 0.5 M H_2SO_4 medium and BFS and BFP in 1 M HCl, and positive for the rest of the inhibitor systems. Negative values of ΔH_{ads} indicate that the adsorption of inhibitor molecules is an exothermic process whereas positive values indicate endothermic nature of the reaction.
9. The entropy values were found to be negative for the following inhibitor systems – CN in both acid medium and positive for the following inhibitor

systems – BF in both acid medium. The negative ΔS_{ads} values can be attributed to the adsorption process which is accompanied by an increase in the order of the system resulting from the associated complex of inhibitor and mild steel. The positive sign of ΔS_{ads} arises from substitutional process which can be attributed to the increase in the solvent entropy and more positive water desorption entropy. This leads to an increase in disorder due to the fact that more water molecules can be desorbed from the metal surface by one inhibitor molecule.

10. The E_{corr} for all the examined inhibitor system in both the acid media do not change appreciably with the addition of the inhibitors and thus affect the anodic dissolution as well as cathodic hydrogen evolution reactions and act as mixed type inhibitors.
11. I_{corr} values decreased significantly in the presence of inhibitors showing that all the inhibitors are effective in controlling corrosion.
12. Tafel constants b_a and b_c for the studied systems and polarization curves of MS in the presence of current inhibitors infer that all the studied inhibitors behaved as mixed type inhibitors.
13. R_p values increased with increase in inhibitor concentration indicating a better corrosion protective ability of the inhibitors under study.
14. The Nyquist plots contain depressed semi-circles with the centre under the real axis, whose size increase with the increase in CN and BF extracts concentration, indicating that the charge transfer process mainly controls the corrosion of mild steel.
15. The impedance parameters for the corrosion of mild steel in acid media without and with addition of various concentration of CN and BF extracts reveal that, R_{ct} values increased but C_{dl} values tends to decrease with increasing concentration of the inhibitor. This behaviour reveals the adsorption of CN and BF extracts on mild steel surface.
16. The morphology of the specimen surface using SEM revealed that in the absence of the inhibitors a corroded rough and coarse uneven surface

developed. However in the presence of the inhibitors, the rate of corrosion is suppressed as can be seen from the smooth surface of the specimen.

17. IR spectral data of corrosion products of the studied systems confirm that the inhibitors are being adsorbed on mild steel surface.

CONCLUSION

- CN and BF extracts act as potential benign inhibitors for the corrosion of mild steel in both acidic media.
- The adsorption of the inhibitors obeys Langmuir and Temkin adsorption isotherms.
- Thermodynamic parameters confirm the strong interaction of the inhibitor with the mild steel surface.
- Tafel studies, linear polarization and impedance studies revealed that the inhibitors act as mixed type inhibitors.
- FTIR studies conducted on corrosion product confirm the formation of CN-Fe complex and BF-Fe complex.
- SEM studies prove the adsorption of the CN and BF extracts on the mild steel surface.

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